Monolayer to bilayer transition in a dipolar system

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We study the transition from a one-dimensional magnetic dipolar monolayer to a bilayer as it is compressed beyond the close-packed condition. The pressure in a close-packed monolayer is found to be nearly independent of the number of dipoles. In the case of weak dipolar interactions, our experimental results indicate that the bilayer formation is governed by short-range steric and electrostatic repulsion, whereas for strong dipolar interactions the bilayer formation is governed by long-range dipolar repulsion.

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I. INTRODUCTION

One-dimensional (1D) systems have intrigued scientists for many years, mainly because they are model systems for their two- and three-dimensional counterparts, and it has been found that the underlying physical models can be solved more easily in one dimension [1]. Such 1D systems are also found in nature, in, e.g., porous rocks or ion channels in the body, and it is therefore of great importance to characterize their behavior [2,3]. In solid state physics recent studies have demonstrated the existence of both short- and long-range ferromagnetic order in one-dimensional atomic chains, thus opening up new avenues to fabricate nanostructures of reduced dimensionality [4]. Despite this interest rather few experimental studies have aimed at studying how one-dimensional systems may undergo phase transitions by taking advantage of extra dimensions, most probably due to a limitation of available model systems. A notable exception is the one considered in Refs. [5–7], where the stability and breakup of dipolar rings is reported. Such systems may help us to understand how quasi-one-dimensional systems undergo conformational changes.

On the other hand, considerable efforts have been put into the study of transitions from two to three dimensions using Langmuir monolayers as model systems [8–10]. From such studies it is possible to obtain valuable information about cracks and folding in presence of different molecular interactions.

Here we aim to study the transition of a dipolar system from a monolayer to a bilayer using a magnetic trap recently introduced by us [11,12]. Our measurements allow us to probe the collapse pressure and detailed pressure isotherms of monolayer and bilayer systems, thus giving useful information on the transition from one to two dimensions.

II. EXPERIMENT

The magnetic trap was created using a bismuth-substituted ferrite garnet film ($Lu_{2.5}Bi_{0.5}Ga_{0.1}Fe_5O_{12}$) of thickness 4 μm and magnetization $M_s \sim 10^5$ A/m grown epitaxially on top of a 0.5 mm gadolinium gallium garnet substrate. We have previously shown that near stress lines the magnetization vector redistributes to form a dipolar line which can be used to trap magnetic beads [12]. Moreover, the garnet film also contains magnetic domain walls, which are directed perpendicular to a stress line. When the walls occur in a pair they may act as magnetic barriers confining the beads along the stress line. A detailed characterization of the magnetic trap was given in Refs. [11,12].

A small cell of diameter 1 cm was put on top of the magnetic film, and beads immersed in deionized, pure water at a density of 10^7 beads/ml were confined within the walls of this ring. The paramagnetic beads of susceptibility $\chi \approx 0.17$ and diameters $2a = 2.8$ μm were coated with a carboxylic acid (COOH—) group (Dynabeads M270). The beads and domain walls were visualized by a Leica polarization microscope used in transmission (the magnetic film is transparent in visible light), and the images were captured by a Hamamatsu charge-coupled device camera. The temperature during the experiments was kept constant at $T = 293$ K. After letting the system equilibrate for 20 min, one observes that the beads reside directly on top of the stress lines. Applying a strong magnetic field H_z in the z direction, we were able to align the magnetic moments of the bead. The distance L between two magnetic barriers can be controlled accurately by applying a small magnetic field H_y parallel to the magnetic film and perpendicular to the stress line. Here $H_y \ll H_z$, and the in-plane field H_y does not influence the magnetic moment of the beads.

Figure 1 shows a schematic drawing where N ($N=4$) beads have been trapped, and their magnetic moments have been aligned in the z direction. The repulsive force F_x from the barrier on the ensemble can be found by measuring the distance between each individual dipole and the barriers. Due to the fast decay of the barrier force it is often enough to measure the distance t to the two closest beads. In equilibrium the magnitude of this force is equal to the dipolar pressure exerted by the magnetic dipoles on the barriers. We thus have a method to find the pressure from the measurement of t and can plot it versus barrier separation L at constant room

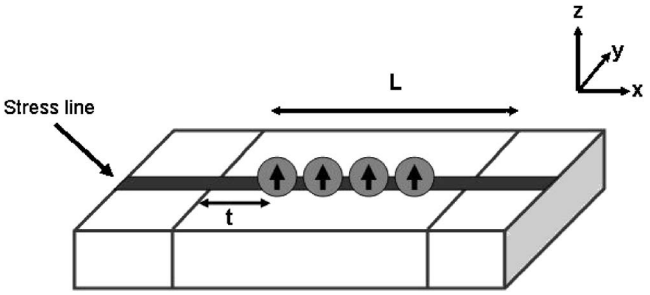

FIG. 1. Schematic drawing of the magnetic trap used here.

temperature. Due to the many steps involved in calibrating the force, we will not repeat this here. Instead we refer the reader to Ref. [11] for details.

Figure 2 shows seven ($N=7$) beads confined between two barriers and gradually compressed from a dilute monolayer to a close-packed bilayer in presence of a magnetic field $H_z=1680$ A/m. In Fig. 2(a) the beads compose a dilute monolayer, whereas in Fig. 2(b) they have been compressed to a close-packed monolayer. The critical pressure P_c where the monolayer starts buckling is found to be $P_c \approx 50$ fN. An early stage of the buckling is shown in Fig. 2(c). Finally, in Fig. 2(d) a close-packed bilayer has formed. We emphasize that the formation of the bilayer is a continuous process, and no snap-through effects are observed. In the following we will develop a model aiming to understand the transition from a monolayer to a bilayer.

III. DISCUSSION

Consider a monolayer consisting of N dipoles, each of radius a separated by a distance d_{ij}. The magnetic moments are aligned along the external magnetic field H_z. The total dipolar energy is then given by a sum over all interactions,

$$E_m = \sum_{j>i}^{N} \sum_{i=1}^{N-1} E_{ij}, \quad E_{ij} = -\mu_0 \boldsymbol{m}_i(r_i) \cdot \boldsymbol{H}_j(r_i). \tag{1}$$

Here μ_0 is the permeability of water, r_i is the position of bead i, and $\boldsymbol{H}_j(r_i)$ is the field acting on particle i from particle j. We will here assume that only the external magnetic field H_z influences the magnetic moment, which then can be

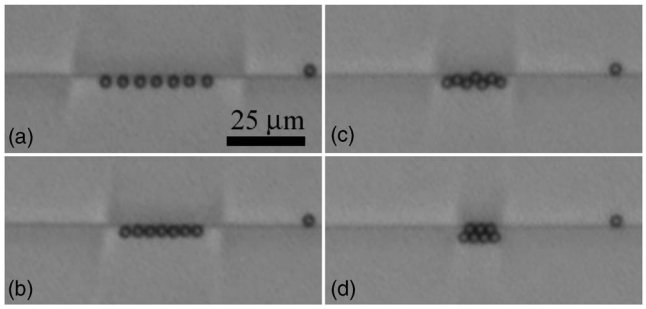

FIG. 2. The figures show seven beads as they are compressed from a monolayer (a), (b) via a buckling region (c) to a bilayer (d). The external magnetic field in the z direction is $H_z=1680$ A/m.

expressed as $\boldsymbol{m}_i=(4\pi/3)a^3\chi H_z \boldsymbol{e}_z$, where $\boldsymbol{e}_z$ is the unit vector in the z direction. The dipolar system is confined between two barriers separated by a distance L, and the distance from one barrier to the nearest colloid is t. If the particles are identical and separated by a distance $d=(L-2t)/(N-1)$, and we assume that only nearest neighbors interact, it can be shown that

$$E_m = \frac{4\pi\mu_0\chi^2 a^6 H_z^2}{9d^3}(N-1). \tag{2}$$

Assume that the distance between the barrier changes with a small distance dL, which means that a work $dW=P_m dL$ is done by the barriers on the dipolar system. Here the change in distance dt between the barriers and the two nearest dipoles is negligible, at least an order of magnitude smaller than dL. Since $dW=-dE_m$, the one-dimensional pressure of the dipole system is found to be

$$P_m = -\frac{dE_m}{dL} = \frac{4\pi\mu_0\chi^2 a^6 H_z^2}{3d^4}. \tag{3}$$

The distance t together with the calibrated force $F_x(t)$ is used as the pressure sensor since the force's magnitude equals the pressure $[P_m=F_x(t)]$ of the dipolar monolayer. The word "pressure" used here is not a quantity related to the size or the statistical behavior of the system. Instead, it reflects the magnitude of the forces acting on the system. The pressure versus length curves that will be presented here are termed pressure isotherms, inspired by the terminology used in Langmuir monolayer research [8]. The word "isotherm" is justified since the temperature is constant in our experiments. It is seen that the dipolar pressure given by Eq. (3) is essentially expressed as $P_m \propto 1/L^4$, which differs substantially from Boyle's law in one dimension, $P=NkT/L$ (k is Boltzmann's constant).

At the close-packed density $d=2a$, and the close-packed dipolar pressure is found to be

$$P_c = \frac{\pi\mu_0\chi^2 a^2 H_z^2}{12}. \tag{4}$$

Upon setting $\chi=0.17$, $a=1.4$ μm, and $H=1680$ A/m, we see that $P_c=53$ fN, which is in excellent agreement with the experimental value obtained for the monolayer consisting of $N=7$ colloids.

Note that according to Eq. (4) the pressure at the close-packed density is independent of the number of beads. If we calculate the dipolar pressure by using Eq. (1) taking into account all the dipolar interactions (not only the nearest neighbors), we instead find that

$$P_c = \frac{\pi\mu_0\chi^2 a^2 H_z^2}{12}\frac{N_{eff}}{N-1}, \quad N_{eff} = \sum_{j>i}^{N}\sum_{i=1}^{N-1}\frac{1}{(i-j)^3}, \tag{5}$$

which depends on the number of beads as long as N is small. In Fig. 3 the solid line displays the theoretical values of P_c/H_z^2 obtained using Eq. (5) with $\chi=0.17$ and $a=1.4$ μm. The squares of Fig. 3 show the measured values of P_c/H_z^2, and it is seen that it is relatively constant for monolayers between $N=5$ and 15. At larger bead number N we note that

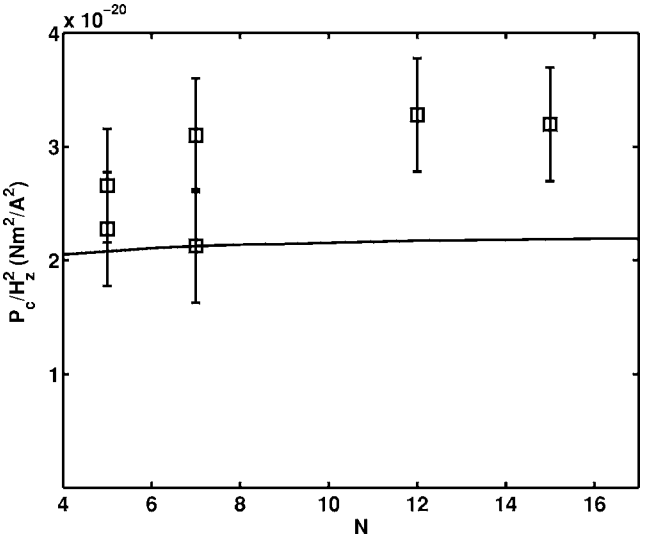

FIG. 3. The critical pressure P_c/H_z^2 as a function of the number of beads N. The solid line is a theoretical curve, whereas the squares show the experimental points.

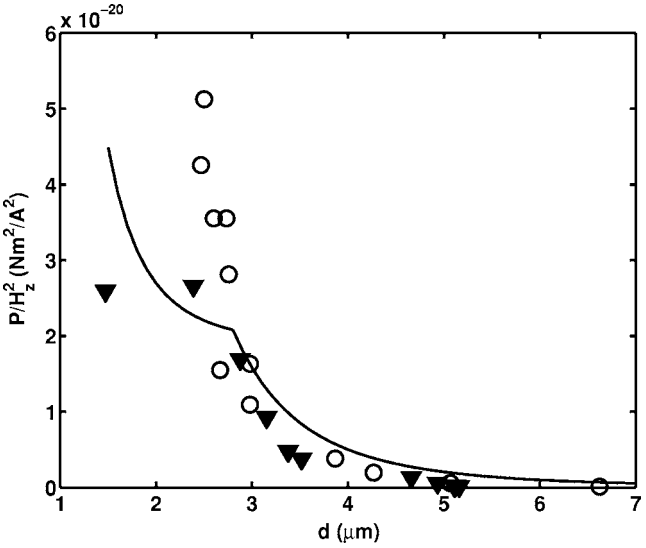

FIG. 4. The pressure (P/H_z^2) versus d for a system composed of $N=7$ (circles) and $N=15$ (triangles) colloids. The solid line is a theoretical fit using Eq. (7).

there is a small discrepancy between the experimental data and theoretical values, which could be related to the approximations required to obtain Eq. (5).

When the monolayer is compressed beyond the close-packed density, Eq. (3) no longer holds. However, to first order, the buckling of the monolayer can be described by adding an extra dipolar energy associated with the interaction of every second dipole

$$E_{m2} = \frac{4\pi\mu_0\chi^2 a^6 H_z^2}{9(2d)^3}(N-2) = \frac{\pi\mu_0\chi^2 a^6 H^2}{18d^3}(N-2). \quad (6)$$

Taking into account this additional repulsive energy, we find the dipolar pressure above and below close-packed density to be

$$P_d = \begin{cases} \dfrac{\pi\mu_0\chi^2 a^2 H_z^2}{12} + \dfrac{\pi\mu_0\chi^2 a^6 H_z^2}{6d^4}\dfrac{N-2}{N-1} & \text{if } d \leqslant 2a, \\ \dfrac{4\pi\mu_0\chi^2 a^6 H_z^2}{3d^4} + \dfrac{\pi\mu_0\chi^2 a^6 H_z^2}{6d^4}\dfrac{N-2}{N-1} & \text{if } d \geqslant 2a. \end{cases} \quad (7)$$

Note that beyond the close-packed condition the pressure term describing the interaction between nearest neighbors is constant and given by Eq. (4). We also emphasize that additional terms are required if we want to describe compression to a trilayer.

Figure 4 shows the pressure (P/H_z^2) versus distance d between the colloids for two monolayers consisting of $N=7$ (circles) and $N=15$ (triangles). In the first case ($N=7$) the applied magnetic field was about $H_z=1680$ A/m, and the dipolar interactions were rather weak (close-packed dipolar pressure $P_c \approx 50$ fN). In the second case ($N=15$) we applied a much stronger magnetic field ($H_z \approx 4680$ A/m), and the dipolar interactions were much stronger here (close-packed dipolar pressure $P_c \approx 700$ fN). The solid line shows the corresponding theoretical fit using Eq. (7).

For both monolayers we observe a good agreement between measurement and theory as long as $d > 2a$. However, when the monolayers are compressed beyond the close-packed condition ($d=2a$) the measured pressure in the monolayer exposed to a weak field ($N=7$) continues to increase, and no signs of a transition were observed in the isotherm. This suggests that long-range dipolar interactions are not responsible for the transition from a monolayer to a bilayer. Instead, it is likely that short-range steric repulsion and electrostatic repulsion play a central role during this transition. This conclusion is reasonable once we remember that the applied magnetic field H_z as well as the corresponding dipolar repulsion was relatively weak. Our measurements suggest that these additional short-range forces, which do not play a role in a dilute monolayer, are comparable to the dipolar pressure when $d=2a$. For increased magnetic fields (triangles of Fig. 4) we found that t did not change substantially as we decreased L, and the pressure remained nearly constant at 700 fN. This may suggest that upon increasing the magnetic field, the dipolar interactions eventually overcome the steric and electrostatic repulsion.

It should be mentioned that t is rather small when the pressure in the dipolar system increases, and that it becomes increasingly difficult to measure F_x with high accuracy. The magnetic force from the barrier on the colloids also put limits on how strong magnetic fields we can apply and still be able to measure the pressure in the buckling region. Thus, it would be of interest to develop a magnetic trap using a material with larger magnetization M_s and therefore larger barrier force on the colloids.

IV. CONCLUSION

We study the buckling and bilayer formation of a one-dimensional magnetic dipolar monolayer as it is compressed

beyond the close-packed condition. We observed that by tuning the dipolar interactions between the colloids in the monolayer we could tune the force required to compress the monolayer into a bilayer. Moreover, the pressure in a close-packed monolayer is nearly independent of the number of beads. Measurements at low magnetic fields revealed the action of nonmagnetic forces responsible for the monolayer bilayer transition.

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